



Overview

- H₂ production technologies and comparative assessments
- Conversion of natural gas
- Catalytic conversion of CH₄
- Reforming Technologies for producing H₂
- Simulation with ASPEN Plus
- Process flowsheet and results summary
- Findings and remarks

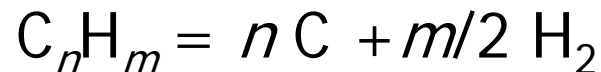
Assessments of H₂ Production Processes

Process	Efficiency (%)	
	Energy	Exergy
Steam Methane Reforming (H/C based)	86	78
Coal gasification (H/C based)	59	49
Current –Technology water electrolysis (Non H/C based)	30	26
Advanced –Technology water electrolysis (Non H/C based)	49	41
Thermo-chemical water decomposition (Non H/C based)	21	19
SMR/current-tech. water electrolysis (integrated)	55	48
SMR/advanced-tech. water electrolysis (integrated)	70	62
SMR/thermo-chemical water electrolysis (integrated)	45	40

M. A. Rosen and D.S. Scott, Intl. J. of Hydrogen v23, n8, pp 653-659

Conversion of Natural Gas

- Conversion of natural gas to generate H_2 has been a challenging issue. The processes may be classified in to two groups: direct and indirect process.
- The general stoichiometric reaction is



- Reaction temperature: 2200-2300 K
- Conducted at atmospheric pressure
- Conversion rate is 70%

Non-catalytic Conversion of CH₄

- Thermal or non-catalytic decomposition of methane requires elevated temperatures (1200-1500°C).
- Special catalysts is required for decomposing methane at relatively low temperatures.
- Prospective catalysts include supported transition metal-based catalysts and metal oxides.
- This effort is based on a three-step approach:
 - reaction engineering,
 - reactor engineering and
 - process engineering.

Thermo-catalytic Conversion of CH₄

- The thermocatalytic decomposition of methane was studied over various catalysts and supports in a wide range of temperatures (500-1000°C)
- Ni- and Fe-containing catalysts demonstrated relatively high efficiency and stability (for several hours) in the methane cracking reaction at moderate temperatures (600-800 °C)

Catalytic Cracking of Methane

- Direct catalytic cracking of CH₄ into H₂(gas) and C(solid) followed by catalyst regeneration in oxidative atmosphere is an attractive alternative



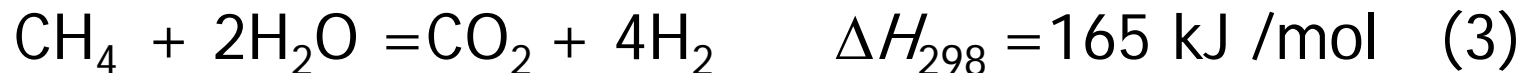
- CO₂ can be separated in time for H₂ production, since in CO₂ are formed during the coke removal from the catalytic surface
- Nickel is known as one of the active catalyst in CH₄ cracking at low temperature (around 500°C)
- Conversion rate of CH₄ to H₂ is 40%-50%

Steam Methane Reforming (SMR)

- Indirect processes which include conversion of CH₄
- Most important and popular chemical process for H₂ generation
- Involves five species in two reversible reactions.



- Overall reaction :

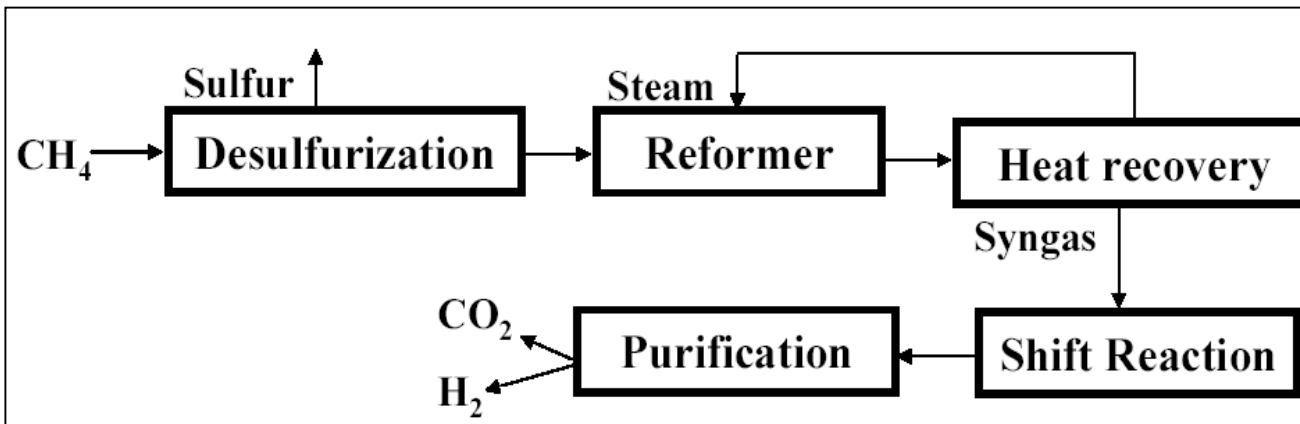


A. Heinzl, B. Vogel, P. Hubner, J. of Power Sources, 105(2002) 202-207

Steam Methane Reforming (SMR)

– 4 Main Steps

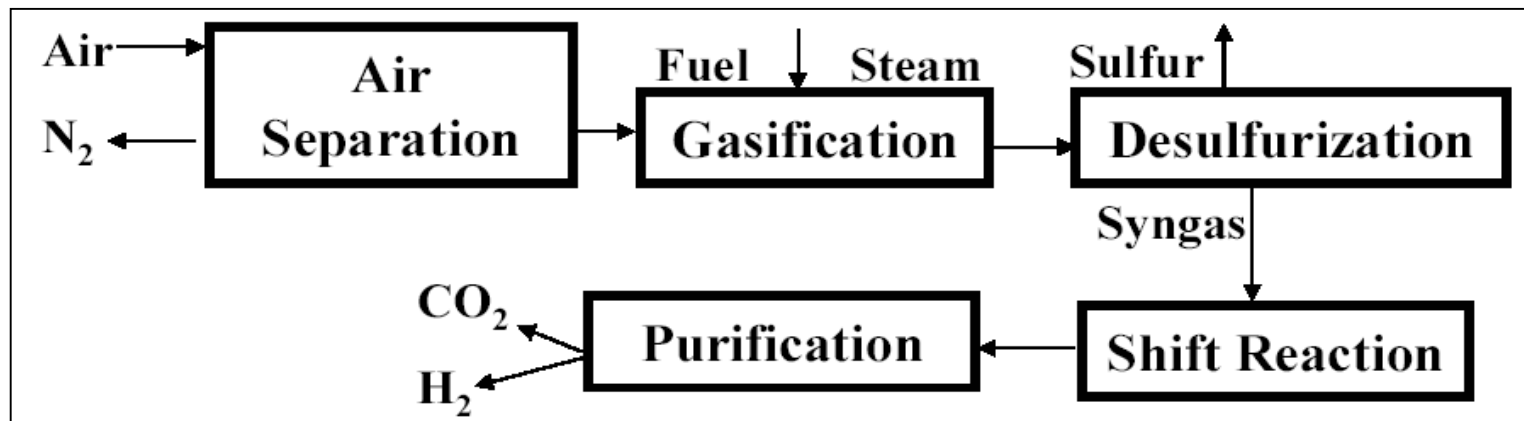
- pretreatment process
- a reformer reactor
- a shift reactor
- gas purification process



Partial Oxidation (POX)

– 4 Main Steps

- pretreatment process
- a reformer reactor
- a shift reactor
- a gas purification process



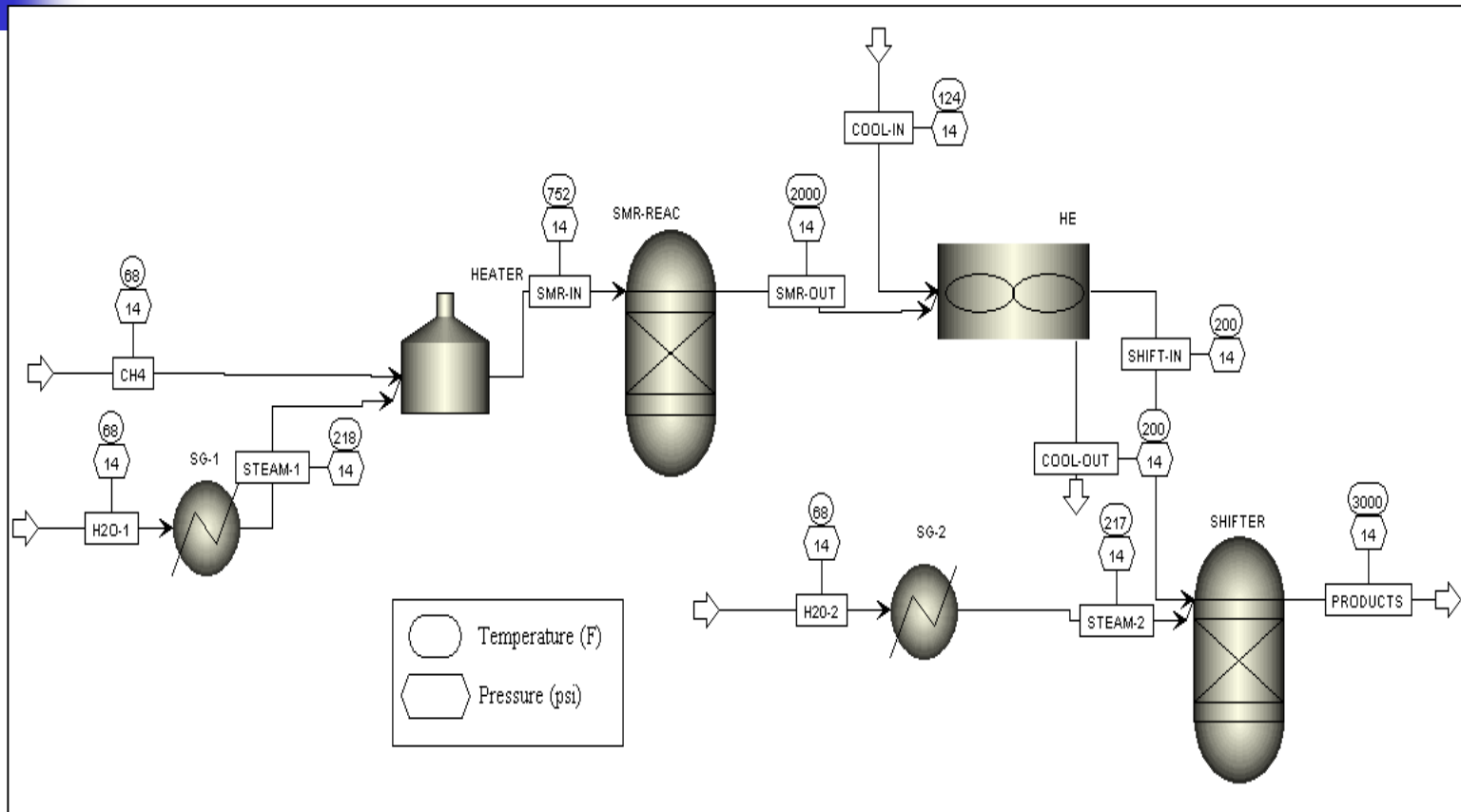
Autothermal Reforming (ATR) Process

- ATR integrates POX with SMR
- ATR have low energy requirement and high gas velocity
- The general reaction mechanism for ATR reactor:

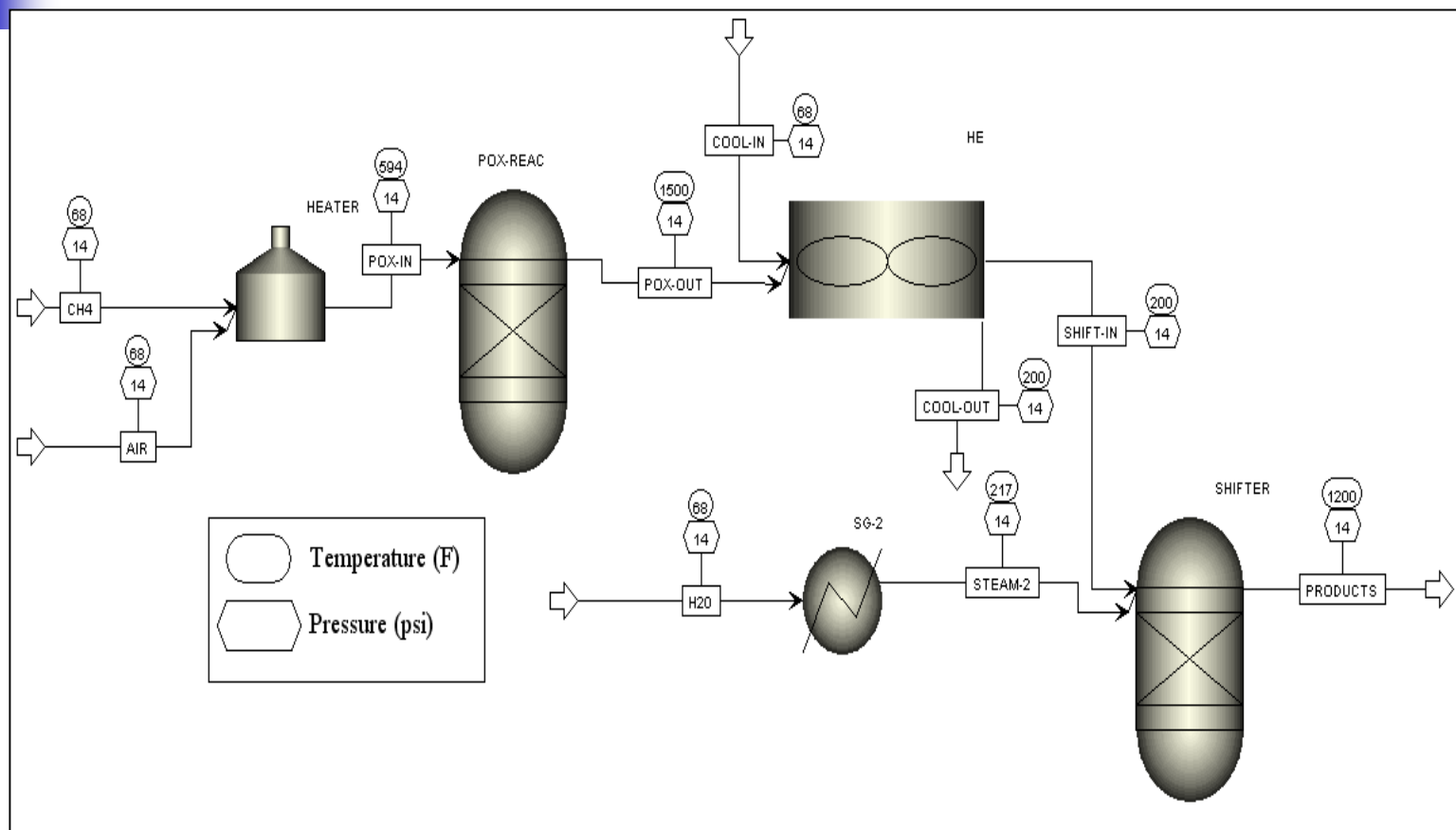
$$\text{CH}_4 + \alpha \text{O}_2 + \beta \text{H}_2\text{O} + 3.77\alpha \text{N}_2 \Rightarrow \text{products}$$
- α is the stoichiometric coeff. varies from 0.0 to 1.0
- β is the stoichiometric coeff. varies from 0.0 to 1.2
- Main process parameters are air ratio, S:C ratio, preheat temperature and reactor pressure.
- H_2 content is much lower due to the dilution of N_2 from the reactant air.

*Y. S. Seo, A. Shirley, S. T. Kolaczowski,
 J. of Power Sources 108(2002) 213-225*

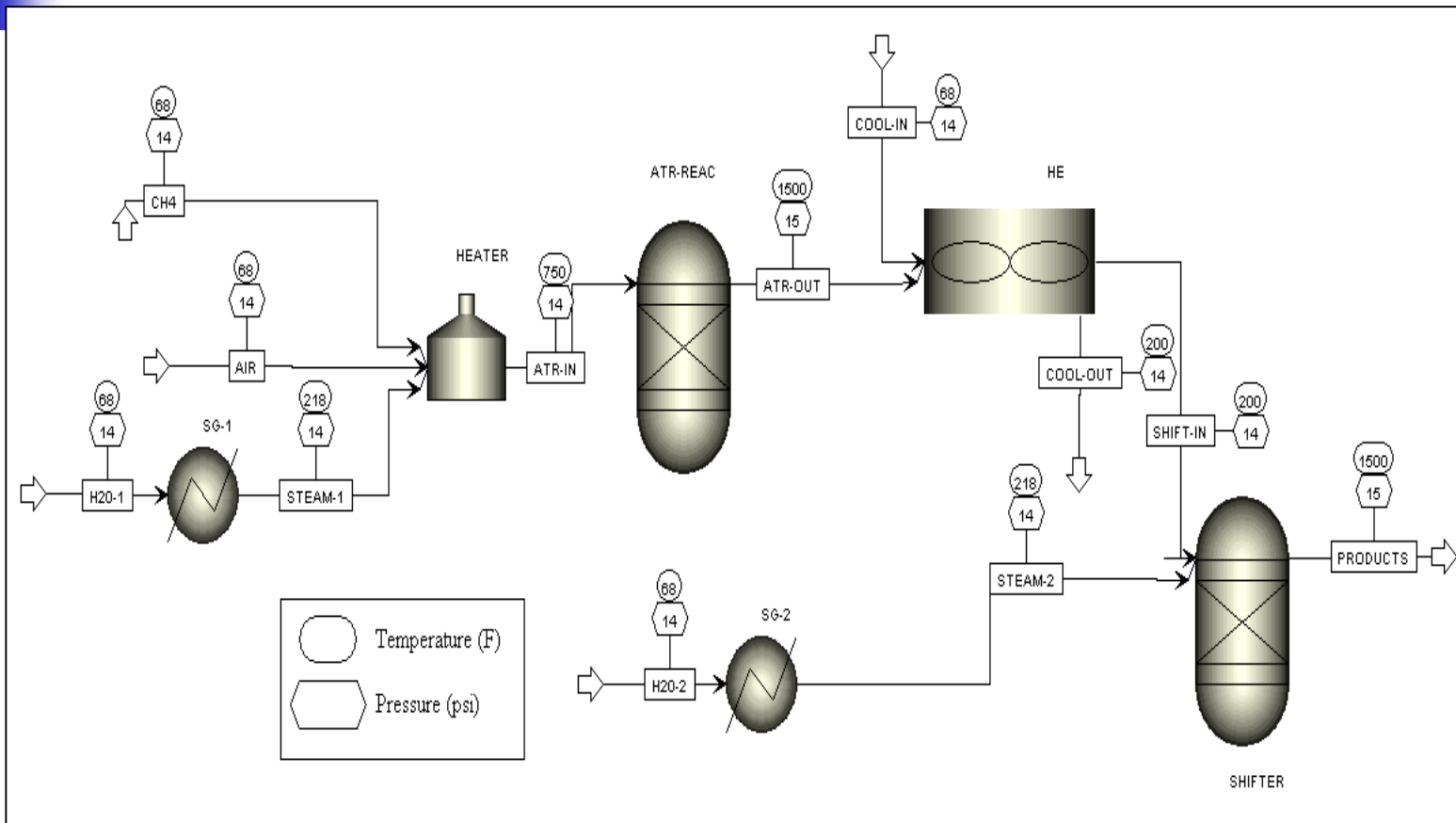
Process Flowsheet- SMR Process



Process Flowsheet- POX Process



Process Flowsheet- ATR Process



Findings and Remarks

- For H_2 generation CH_4 can be reformed by SMR, POX or the ATR processes
- Thermodynamic equilibrium can be reached in all cases
- ATR process is more flexible than SMR for start-up and load change
- SMR reforming system has the highest CH_4 and POX system has the lowest CH_4 consumption.
- POX reforming system is superior to the other systems in terms of the energy cost to produce the same amount of hydrogen from CH_4



Sulfur-Iodine Cycle

- Work is beginning on the inputting of this cycle into ASPEN-PLUS.
- Little progress has been made to this point.

Progress with Cycle Literature Survey

- Found 93 new references. 37 refer to S-I and UT-3.
- Through these references two new cycles have been identified.
- NERI database has been checked. Corrections, ranging from minor to significant, have been made.
- About a dozen cycles have been identified that are not in the database.



Simulation of Reactor Flow

- In this project, hydrogen is generated by decomposing methane at a high temperature (~ 2000 K) inside the solar thermal reactor.
- The chemical reaction is
$$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \quad \Delta H_{298\text{K}} = 75 \text{ kJ/mol}$$
- Several parameters have been defined, including dimensions and information on the porous medium.
- Materials: inner cylinder-graphite, outer-quartz.



Parameter Calculation

Permeability

$$\alpha = \frac{D_p^2 \epsilon^3}{150(1-\epsilon)^2}$$

Inertial Resistance Coefficient

$$c_2 = \frac{3.5(1-\epsilon)}{D_p \epsilon^3}$$

where

α - Permeability, m²

ϵ - Porosity

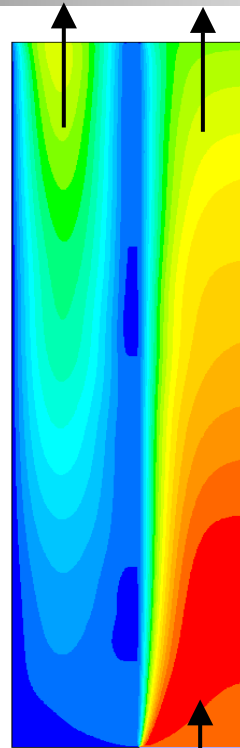
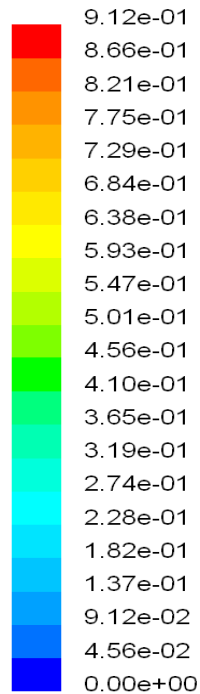
D_p - Pore diameter, m



Current Work

- Analyze velocity, temperature, pressure under selected pore diameters.
- Analyze hydrodynamics of the flow.
- Analyze pressure drop after the flow passes through porous medium.

Velocity Contours of Reactor

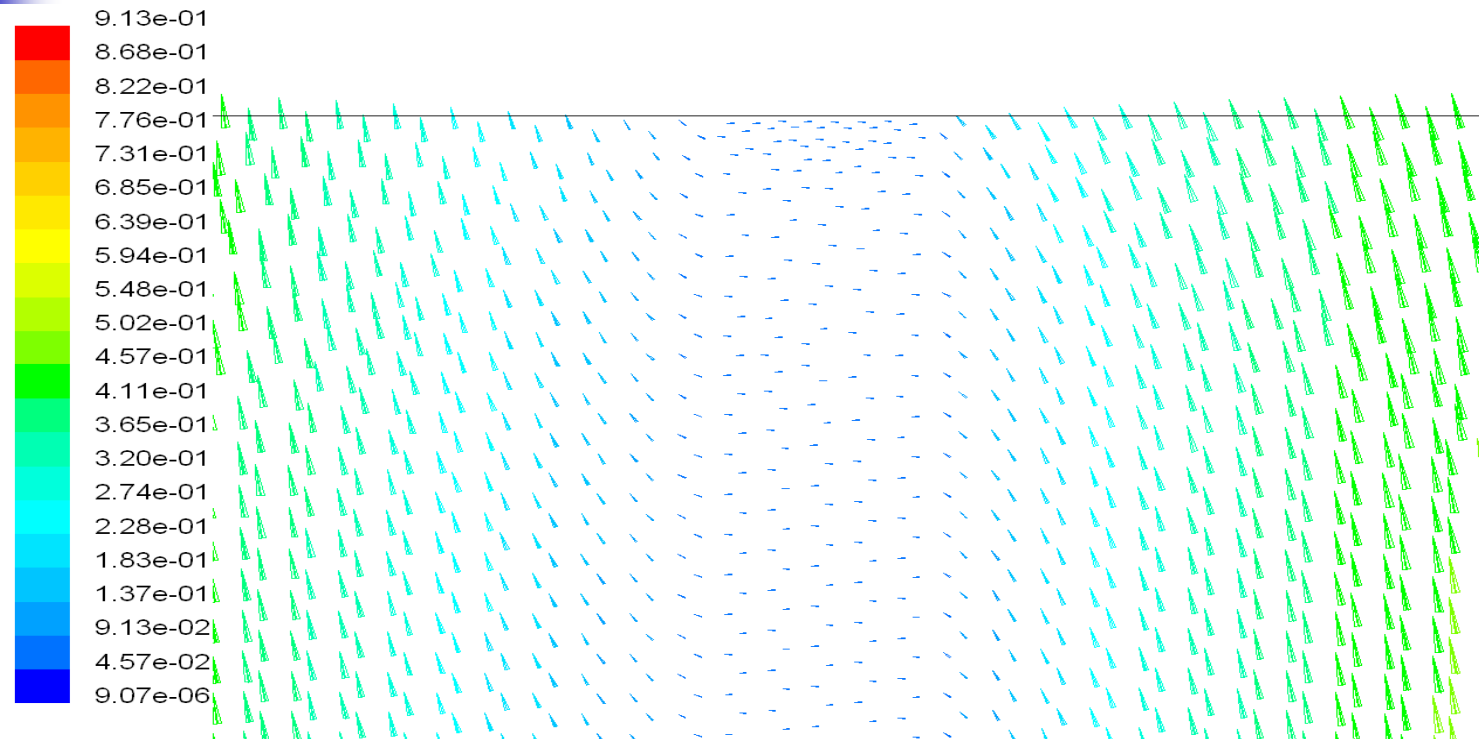


Contours of Velocity Magnitude (m/s)

FLUENT 6.1 (2d, dp, segregated, spe5, lam)

Mar 02, 2004

Velocity Vectors of Reactor



Velocity Vectors Colored By Velocity Magnitude (m/s)

Mar 02, 2004
FLUENT 6.1 (2d, dp, segregated, spe5, lam)

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Basic System Design Issues

- Initial design developed will be driven by a dish system unit, irrespective of what is deemed most appropriate for production. One at UNLV can be used.
- Two general approaches are to have a reactor on the unit (less likely) or the reactor ground based near the unit.



Basic System Design Issues (Cont.)

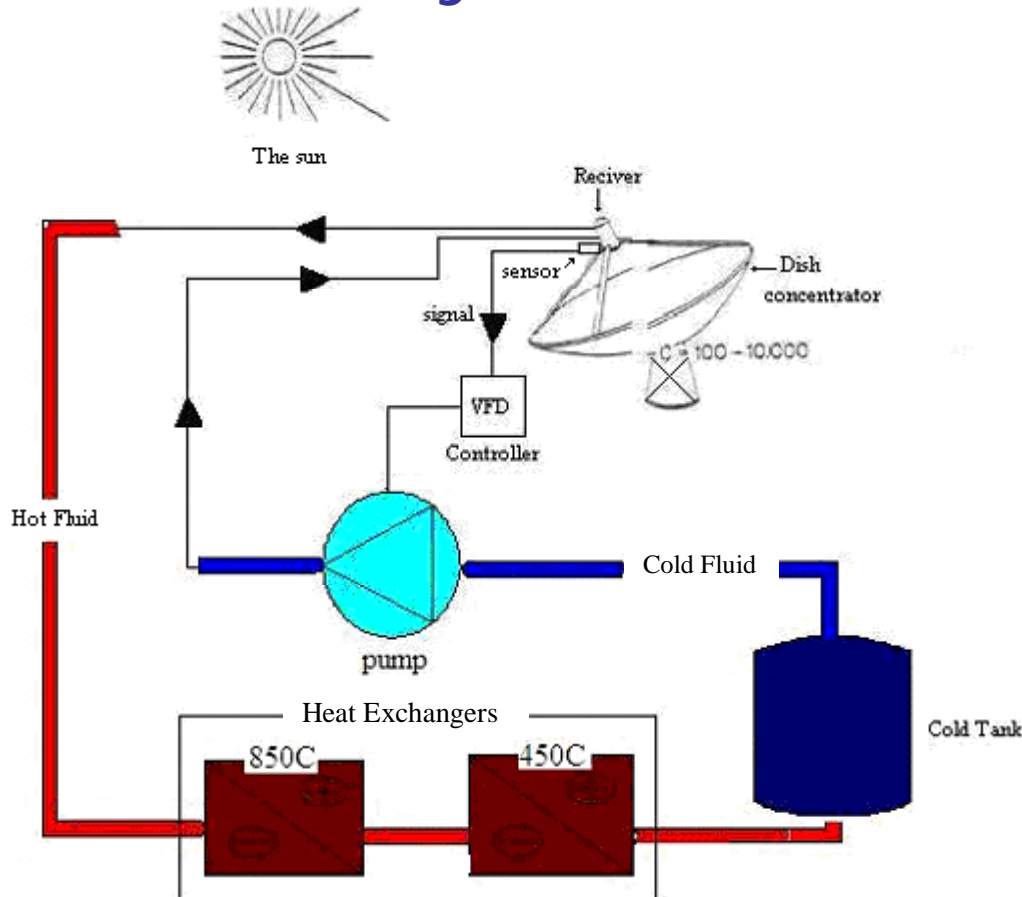
- Two fluids are being considered: molten salt and air.
- A great deal of experience has been logged with both types of fluids.
- For the initial design, air is currently the most probable candidate.



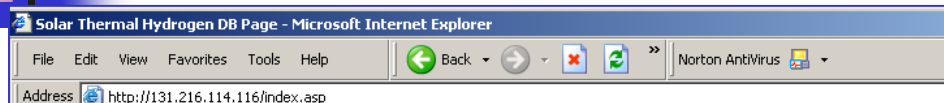
Basic System Design Issues (Cont.)

- A ground-based heat exchanger and reaction chambers will be included.
- Supplemental heat will be available.
- Careful calibration simulations of the unit will allow easy evaluations of design changes and scale-up.

A Possible System



Automatic Scoring Process



Administrator Login

Login ID:

Password:



- Scoring Process**
- [Scoring Page](#)
- Search**
- [PID](#)
- [Reaction Code](#)
- [Reference Code](#)
- [Author](#)
- Data**
- [Add Cycle](#)
- [Add Reaction](#)
- [Add Reference](#)
- [Edit Cycle Record](#)
- [Edit Reaction Record](#)
- [Edit Author Record](#)

Search Criteria

Please select solar collector type (for weighting purpose)

- ☒ Trough
 ☐ Dish
 ☐ Standard Tower
 ☐ Advanced Tower

Please select the criteria for scoring:

- | | |
|---|---|
| <input type="checkbox"/> 1. Number of chemical reactions | <input type="checkbox"/> 9. Compatible with thermal transients and/or diurnal storage |
| <input type="checkbox"/> 2. Number of separation steps | <input type="checkbox"/> 10. Number of papers |
| <input type="checkbox"/> 3. Number of chemical elements | <input type="checkbox"/> 11. Scale of test |
| <input type="checkbox"/> 4. Use abundance chemical elements | <input type="checkbox"/> 12. Efficiency and/or cost figures |
| <input type="checkbox"/> 5. Employ non-corrosive Chemicals | <input type="checkbox"/> 13. Chemical that toxic to people |
| <input type="checkbox"/> 6. Degree of solids flow | <input type="checkbox"/> 14. Chemical that long term toxic to people |
| <input type="checkbox"/> 7. Use of radiant heat transfer to solids | <input type="checkbox"/> 15. Chemical that non environmentally toxic |
| <input type="checkbox"/> 8. High temperature endothermic step be compatible with the best selected technology above | <input type="checkbox"/> 16. Chemical that not reactive with air or water |

Please enter the minimum score: (scale 0-100)
 *** Scoring results is shown in descending order ***

- Prototype web-based automatic scoring system (131.216.114.116)

- Utilizes the Internet Information Service, Active Server Page, MS ACCESS, SQL language and MS VB.

- Scoring system is protected by password and IP restriction.




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Automatic Scoring Process (contd.)

Solar Thermal Hydrogen DB Page - Microsoft Internet Explorer

Address: http://131.216.114.116/index.asp



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SOLAR THERMAL CHEMICAL HYDROGEN
GENERATION
Sponsored by Department of Energy

Solar Thermal Generation Type = TROUGH Cutoff = 35

pid	Cri#1	Cri#2	Cri#3	Cri4	Cri#5	Cri#8a	Cri#10	FINAL SCORE
2	10	10	5	7	10	0	2	37
7	10	10	10	10	8	0	3	36
21	7	10	8	7	5	7	0	39
31	7	10	5	4	3	10	1	41
52	3	10	10	4	10	8	1	42
77	10	10	2	8	10	0	2	38
106	10	10	10	9	10	0	1	38
131	0	10	10	4	10	10	0	42
133	0	10	8	4	10	9	0	40
139	0	10	5	4	10	9	0	40

Scoring Process

[Scoring Page](#)

Search

[PID](#)

[Reaction Code](#)

Reference Code

Author

Data

[Add Cycle](#)

[Add Reaction](#)

[Add Reference](#)

[Edit Cycle Record](#)

[Edit Reaction Record](#)

[Edit Author Record](#)

- The current scoring system takes criteria identified from criteria list, 1,2, 3, 4, 5, 8 and 10.
- Some criteria require manual identification and will be discussed in detail by Sean.

Search Engine - Cycle (Primary ID) search

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 Reference Code
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 Data
[Add Cycle](#)
[Add Reaction](#)
[Add Reference](#)
 Edit Cycle Record
 Edit Reaction Record
 Edit Author Record

Search PID:
 Please input PID #:

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 Reference Code
 Author
 Data
[Add Cycle](#)
[Add Reaction](#)

Search PID Result
 PID#: 35
 Cycle Name: Osaka Inst. of Tech. (Japan) 1975
 Elements: Ba,I,C,N
 Num of Steps: 3
 Max Temp in C: 0
 Reaction Code: NH4I electrochem
 Reaction Code: BaCO3
 Reaction Code: BaI2

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 Reference Code
 Author
 Data
[Add Cycle](#)
[Add Reaction](#)
[Add Reference](#)

Search Reaction Code Result
 Reaction Code: NH4I electrochem
 Formula: $2\text{NH}_4\text{I} \rightarrow 2\text{NH}_3 + \text{I}_2 + \text{H}_2$
 Temp C: 0
 Pressure (MPa): 0
 Type: hydrogen generation
 Voltage:

Certain search functions
have been implemented!

Data Management

- Cycle Update



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[Author](#)

Data

[Add Cycle](#)

[Add Reaction](#)

[Add Reference](#)

[Edit Cycle Record](#)

[Edit Reaction Record](#)

[Edit Author Record](#)

Add Cycle (* = Required Field) PID: 299 (auto generated)

Cycle Name: * Class:

Reaction Code*

1. <input type="text"/>	2. <input type="text"/>	3. <input type="text"/>
4. <input type="text"/>	5. <input type="text"/>	6. <input type="text"/>

Maximum Tempature: <input type="text"/>	Efficiency: <input type="text"/>
Min. Mass: <input type="text"/>	Max. Mass: <input type="text"/>
Seperation Steps: <input type="text"/>	Conditions: <input type="text"/>

Radiant Heat Transfer to Solids: * Test Scale:

Efficiency/Cost Figures: *

Detail cost calculations from one source

Flow of Solids: *

Comments:

The interface also serves as a Data Management System that can be used to update the data, create new cycle/reaction simply from any web browser!
(MAC machine ???)